



Prediction of Compressive Strengths in Cement-Natural Pozzolan Blends

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Abstract : In this paper, it is aimed to propose prediction approaches for the 2, 7, 28, 90 and 180 days compressive strength of blended cements with natural pozzolan (PZ) by using soft computing techniques. Plant data were collected for the chemical and physical properties of the cement that were used in model construction and testing. The training and testing data were separated from the complete original data set by the use of Multiple Linear Regression (MLR) model based on the training data of the cement strength was created. The importance of chemical mineralogical of clinker, the reactive silica of pozzolan and the water-to-cement ratio were pointed out. The benefit of the model is in the potential ability to control processing parameters to yield the desired strength levels and in providing information regarding the most appropriate experimental conditions to obtain maximum compressive strength.

Key words : compressive strength, blended cement, natural pozzolan, Multiple Linear Regression.

Introduction and Experimental:

The compressive strength of cement is the main property characterizing its classification and influencing its quality [1-2]. The development of strength is affected by many factors, such as cement composition, fineness and water-to-cement ratio w/c. In this case the Multiple Linear Regression (MLR) was the technique chosen to predict the final strengths of cements mixed by natural pozzolan because we have been based on the assumption that each of these factors affects the mechanical properties of hydrated products.

The use of mineral admixtures as partial replacement for Portland cement in blended cements and concrete has become almost unavoidable due to energy-savaing concerns and other environmental considerations [3-4-5]. Pozzolans are siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious properties [6-7-8]. When finely ground, they react in the presence of water at ambient temperatures with dissolved calcium hydroxide (Portlandite $\text{Ca}(\text{OH})_2$) from lime or Portland cement clinker to form strength developing calcium silicate and calcium aluminate compounds [9-10-11]. The chemical and physical properties of natural pozzolan used in our case are presented in table 1.

Twelve blended cements were obtained by grinding the samples of clinkers having different rates of free lime, variable amounts of natural pozzolan and 5% of gypsum in laboratory ball mill to a target SSB $4500\text{g}/\text{cm}^2$. Table 2 shows the main constituents of blended cements and table 3 summarizes the compressive strength development at different hydration ages (2, 7, 28, 90 and 180 days)

Table 1: chemical and physical properties of natural pozzolan

Requirements	natural pozzolan PZ
(SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃)%	46,17 + 13,56 + 5,88
SO ₃ %	0,07
CaO %	10,30
MgO %	2,96
K ₂ O %	2,45
Na ₂ O %	1,03
TiO ₂ %	2,52
P ₂ O ₅ %	0,46
Mn ₂ O ₅ %	0,15
Loss on ignition LOI %	14,38
Reactive silica RS %	33,32

Table 2: constituents of blended cements

Blended cement	%fCaO in cement	%RS in cement	%C ₂ S in cement	%C ₃ S in cement	w/c in cement
1	2,54	5	15,83	42,12	0,28
2	2,24	8,33	13,97	37,16	0,3
3	1,94	12,66	12,1	32,21	0,31
4	1,64	15	10,24	27,25	0,33
5	3,37	5	16,98	40,43	0,29
6	2,98	8,33	14,99	35,67	0,31
7	2,58	12,66	12,98	30,91	0,32
8	2,18	15	10,99	26,16	0,37
9	4,23	5	16,75	39,44	0,3
10	3,73	8,33	14,78	34,8	0,33
11	3,24	12,66	12,81	30,16	0,34
12	2,74	15	10,84	25,52	0,39

Table 3: compressive strengths of blended cements at 2, 7, 28, 90 and 180 days

BC	S _{2d}	S _{7d}	S _{28d}	S _{90d}	S _{180d}
1	23,86	36,75	45,15	54,8	59,45
2	22,17	35,03	42,33	50,19	56,1
3	18,6	30,66	40,26	49,28	54,8
4	11,4	14,93	25,8	35,43	42,9
5	14,83	28,75	38,98	47,08	53,17
6	20,45	32,63	39,73	48,28	56,7
7	16,63	25,48	34,9	46,6	52,95
8	10,03	13,18	23,74	30,88	36,9
9	14,1	26,2	32,43	44,95	51,02
10	15,04	26,8	33,19	46,28	53
11	15,3	25,43	31,9	44,65	51,5
12	8,93	10,88	15,55	21,43	18,75

Bd : blended cement

S_{2d}: compressive strengths at 2 daysS_{7d}: compressive strengths at 7 daysS_{28d}: compressive strengths at 28 daysS_{90d}: compressive strengths at 90 daysS_{180d}: compressive strengths at 180 days

The uncombined lime in the clinker was determined by acidimetric method using $(\text{CH}_2\text{OH})_2$ [12].

Standard consistency of cements was determined using a Vicat apparatus according to the European standard EN 196-3[13]. The expansion was measured according to the LeChatelier method. Compressive strength measurements were conducted at the ages of 2, 7, 28, 90 and 180 days on mortar specimens (dimensions $40 \times 40 \times 160$) prepared and tested in accordance with the European standard EN 196-1 [14].

The reactive silica (RS) of pozzolan was determined according to the established procedure of chemical treatment of the samples with concentrated HCl (36-37% w/w) and KOH in accordance with the European standard EN 196-2[15].

It 's well known that pozzolanic mineral components originate from industrial (e.g. fly ash, silica fume) as well as natural sources (e.g. volcanic ash, trass). Most pozzolanic materials react quite slowly, so that the early strength is diminished significantly [16]. Thus the natural pozzolans especially their reactive silica is effective in reducing the concentration of portlandite coming from the hydration of free lime (fCaO), and because of R-Silica activation, the microstructure of cement paste has been modified [17-18]. The hydration products, especially CSH together with C_2ASH_8 are distributed more homogeneously filling the pores, thus contributes to a greater extent to the development of the mechanical resistance of these blended cements [19-20-21].

Obviously alite C_3S is the main mineral in Portland cement clinker and is the phase, which produces the most relevant cement property. It reacts fast and reaches high strength in a short time. Alite improves both early and late strength potential of the clinker [22-23]. Belite C_2S is less reactive than alite and contributes to late strength (> 28 d); it does not contribute to early strength [23-24].

Most of the time, clinker contains always some free lime but with an excessive high amount of free lime a lower late strength, expansion problems and storage problems can occur [25].

As we have previously detailed, to control processing parameters to yield the desired strength levels, the importance of chemical mineralogical of clinker especially its C_3S and C_2S also reactive silica of natural pozzolan and the water-to-cement ratio w/c were pointed out. Thus the training and testing data were separated from the complete original data set by the use of Multiple Linear Regression (MLR) [26-27].

Results and Discussion

1. MLR Model construction:

Table 4 shows the input and output characteristics of parameters which are used in the Multiple Linear Regression models. The treatment of the stepwise regression data of all the cement characteristics and the experimental results of the compressive strength at the different ages, were conducted by SPSS software.

Table 4: Average characteristics of input and output MLR models data

	Variable	Minimum (%)	Maximum (%)
Input variables	RS	5	15
	fCaO	1.64	4.23
	fCaOxRS	12.7	41.1
	w/c	0.29	0.39
	$\text{C}_2\text{Sx}\text{C}_3\text{S}$	276,64	686,50
	C_2S	10,24	16.98
Output variables	C_3S	25,52	42.12
	S_2d	8,93	23.86
	S_7d	10,88	36.75
	$\text{S}_{28\text{d}}$	15,55	45.15
	$\text{S}_{90\text{d}}$	21,43	54.8
	$\text{S}_{180\text{d}}$	18,75	59.45

The functions developed by the MLR will be used to produce cements compressive strengths at 2, 7, 28, 90 and 180 days. The execution of the stepwise regression MLR statistical processing of data is allowed to screen all input factors and to select those that have a significant effect on responses. The different combinations of these variables were selected to intuitively take into account all the variables in the global model, in order to eliminate one by one, those variables corresponding to the smallest value of the Student test "t", represented by "p-value" (p-value < 0,05). Accordingly, the MLR algorithm was used to select from among the input variables, which one can provide the greatest reduction of the residual variance of the dependent variables. In other words, these variables have the highest partial correlation with the response Y (compressive strengths at 2, 7, 28, 90 and 180 days).

The coefficients forming the compressive strengths models of the cements are listed in table 5. Moreover, the results in the table 5 estimate the significant parameters by the maximum likelihood and according to the probability values (p-value < 0,05). So, they reveal that there are four variables truly significant in the multivariate models for predicting compressive strengths at 2, 7, 28, 90 and 180 days. Therefore, the algorithm of the model MLR is systematically removed the variables whose its significance is too low, compared to the resistance of 2 to 180 days at each stage. The non-selected variables in the three models are shown in table 6.

Table 5: Coefficients forming the five models corresponding to compressive strengths at different ages

compressive strength prediction model at	Time (days)	Input variables	fCaO	C ₃ S	w/c	fCaOxRS	C ₂ S	C ₂ SxC ₃ S
	2	2	Coefficients	-5,8	1,3	-84,6	0,6	-
t			-5,2	7,9	-3,8	3,8	-	-
p-value			0,0009	0,0000	0,0056	0,0055	-	-
7		Coefficients	-7,1	2,1	-165,0	1,0	-	-
		t	-4,5	9,5	-5,3	4,5	-	-
		p-value	0,002	1,2704E-05	0,0008	0,0021	-	-
28		Coefficients	-	3,5	-200,1	-	5,7	-0,2
		t	-	7,3	-4,7	-	2,5	-4,4
		p-value	-	8,1715E-05	0,002	-	0,03	0,002
90	Coefficients	-	3,8	-259,4	-	9,9	-0,3	
	t	-	8,5	-6,5	-	4,7	-6,6	
	p-value	-	2,9305E-05	0,0002	-	0,001	0,0002	
180	Coefficients	-	4,5	-361,3	-	14,8	-0,4	
	t	-	7,1	-6,4	-	5,0	-6,5	
	p-value	-	9,737E-05	0,0002	-	0,001	0,0002	

Table 6: Variables excluded in the five MLR models

Time (days)	compressive strength prediction model at									
	2		7		28		90		180	
Variables	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value
C ₂ S	1,75	0,14	2,65	0,05	-	-	-	-	-	-
RS	-0,98	0,36	-1,31	0,24	-1,35	0,24	0,31	0,77	0,23	0,83
C ₂ SxC ₃ S	-1,69	0,14	-0,93	0,39	-	-	-	-	-	-
RS	-	-	-	-	-	-	-	-	-	-
f-CaOxRS	-	-	-	-	2,23	0,07	1,76	0,12	0,16	0,88
f-CaO	-	-	-	-	-1,48	0,18	0,82	0,45	0,82	0,45

Table 7: Statistical models validation data

Measurement time of the compressive strengths (days)	R ² (%)	Standard error of the estimate
2	99.19	1.82
7	99.88	1.85
28	99.70	2.47
90	99.79	2.57
180	99.68	3.47

2. Statistical model validation tests:

The model validation was carried out by the coefficients of multiple determination test (R²) and Fisher test, which were calculated from the data indicated in the table of the Multivariate Analysis Of Variance (MANOVA) (table 7). The data results of these tests are significant because that the R-squared (R²) values are 99.19; 99.88, 99.70, 99.79 and 99.68% for cement compressive strengths at 2, 7, 28, 90 and 180 days, respectively. So we conclude that the global significance of the models is good. Thus, the resulting models have excellent predictive qualities (table 7).

Consequently; the five equations of the MLR regression are very preventative and they record that the variables forming the prediction equation of the compressive strengths at 2, 7, 28, 90 and 180 days contribute in a very reproducible way in the cement compressive strengths variable score at these five ages. The maximum error data of those five equations are 1.82; 1.85, 2.47, 2.57 and 3.47. The functions generated by the MLR algorithm presenting the best results of predicting cement compressive strengths at 2, 7, 28, 90 and 180 days according to the cement characteristic, are given in the equations (1), (2), (3), (4) and (5).

$$Y_2 = -5,79fCaO + 1,29C_3S - 84,56w/c + 0,61fCaOxRS \quad (1)$$

$$Y_7 = -7,05fCaO + 2,14C_3S - 164,98w/c + 1,0fCaOxRS \quad (2)$$

$$Y_{28} = 5,72C_2S + 3,52C_3S - 200,1w/c - 0,21C_2SxC_3S \quad (3)$$

$$Y_{90} = 9,87C_2S + 3,77C_3S - 259,41w/c - 0,29C_2SxC_3S \quad (4)$$

$$Y_{180} = 14,77C_2S + 4,49C_3S - 361,31w/c - 0,4C_2SxC_3S \quad (5)$$

The variation of Fisher test associated to those five models is significant (p-value < 0,001). Therefore, these models explain a significant proportion of the variables variance of the cement compressive strength at 2, 7, 28, 90 and 180 days.

The analysis of the results of the Fisher test "F" (table 8) showed that the developed models are very significant. Indeed, the "F" values of the cement compressive strength models at 2 to 180 days are equal to 245.8, 331.8, 509.6, 963.5 and 623.8, respectively and they are significant at p-value < 0,001. Those results

indicate that we have less than 0.1% chance of being wrong in claiming that the models contribute better to predict the compressive.

Table 8: MANOVA data

	Compressive strength prediction model at (days)									
	2		7		28		90		180	
	F	p-value	F	p-value	F	p-value	F	p-value	F	p-value
Regression	245,8	1,3E-07	331,8	4,7E-08	509,6	1,0E-08	963,5	1,1E-09	623,8	5,2E-09

Table 9: Experimental models

compressive strength prediction model at	Time (days)	N° experience	RS	fCaO	C ₃ S	w/c	fCaOxRS	C ₂ S	C ₂ SxC ₃ S	measured value	calculated value	deviation calculated e _r
	2	1	5	2,78	33,49	0,32	26,82	13,61	466,88	16,19	15,95	0,25
7	25,64									25,56	0,08	
28	36,84									35,66	1,18	
90	38,22									39,32	-1,10	
180	48,77									48,94	-0,17	
2	2	6	3,1	44,2	0,3	18,6	16,3	389,74	25,26	24,1	0,34	
7									41,8	43,4	-1,57	
28									43,5	45,3	-1,81	
90									35,4	34,8	0,57	
180									43,6	45,5	-1,88	

e_r: the absolute value of the difference between the calculated value and the measured value

3. Models experimental validation:

The validation of the cements compressive strengths model at 2, 7, 28, 90 and 180 days was conducted by established experimental development of 2 mortars cements for each age.

The results of the validation test of the five functions are shown in table 9 and this test consists to measure the deviation between the calculated values of the compression strength which are deducted from the mathematical equations and the experimentally measured value. This gap must be less than or equal to the standard error calculated for each model.

The results presented in table 9 show that the variability explained by models 1, 2, 3, 4 and 5 are experimentally reliable and predictive, since the calculated differences between the compressive cement strength calculated from the established mathematical equations and those measured by the traditional method are always less than the error related to the established model and which are equal to 1.82; 1.85, 2.47, 2.57 and 3.47 for the model of 2, 7, 28, 90 and 180 days, respectively.

Feasibility tests of these laboratory scale models revealed that the exploited models are very promoters and they are useful tools to prevent the compressive cement strength at any age and with the minimal error.

Conclusion:

Most of previous studies are insisting on reactive silica to develop the performance of blended cements. The compressive strength at different ages can be successfully described through the multiple linear regression model used here, considering the specific surface area as independent variable because we've chosen all cements having similar fineness but some varying parameters as C₃S, C₂S, fCaO, w/c and R-Silica were considered as the input variables for the developed strengths.

In the present study results were obtained with the MLR model for the compressive strengths 2, 7, 28, 90 and 180 days with correlation coefficients of 99.19; 99.88, 99.70, 99.79 and 99.68% respectively. thus the

MLR algorithm presenting the best results of predicting cement compressive strengths at 2, 7, 28, 90 and 180 days in the equations (1), (2), (3), (4) and (5).

$$Y_2 = -5,79fCaO + 1,29C_3S - 84,56w/c + 0,61fCaOxRS \quad (1)$$

$$Y_7 = -7,05fCaO + 2,14C_3S - 164,98w/c + 1,0fCaOxRS \quad (2)$$

$$Y_{28} = 5,72C_2S + 3,52C_3S - 200,1w/c - 0,21C_2SxC_3S \quad (3)$$

$$Y_{90} = 9,87C_2S + 3,77C_3S - 259,41w/c - 0,29C_2SxC_3S \quad (4)$$

$$Y_{180} = 14,77C_2S + 4,49C_3S - 361,31w/c - 0,4C_2SxC_3S \quad (5)$$

Finally, from the interpretation of the model, this result could be used of others blended cements having admixtures as partial replacement for Portland cement as silica fume (SF) or fly ash (FA).

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